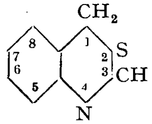
# 63. *Thiazinocyanines. Part II. Cyanines containing the Dihydro-*1 : 3-*thiazine Nucleus.*

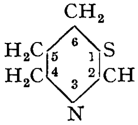
By Frances M. Hamer and Russell J. Rathbone.

2-Thioldihydro-1 : 3-thiazine was converted into its methyl and ethyl derivatives. Alkiodides of these were condensed with heterocyclic quaternary ammonium salts to give simple cyanines of various new types. 2-Methyldihydro-1 : 3-thiazine was prepared by a new method and its alkiodides were used as the starting point for synthesising symmetrical and unsymmetrical carbocyanines. Absorption maxima of the various dyes were compared. The effect of replacing the thiazoline by the dihydro-1 : 3-thiazine nucleus is to produce a bathochromic shift.

After carbocyanines containing the 2 : 4-benzthiazine nucleus (I) had been prepared by use of derivatives having a reactive group in the 3-position (Beilenson and Hamer, J., 1942, 98), the idea of preparing cyanines containing the simple dihydro-1 : 3-thiazine nucleus (II) followed (named originally "Penthiazolin" by

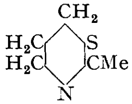
(I.)





(II.)

Gabriel and Lauer, *Ber.*, 1890, **23**, 87). For cyanine syntheses the 2-methyl derivative (III) and 2-thiol-derivative (IV; R = H), which are known, seemed promising starting points.



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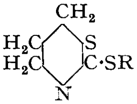

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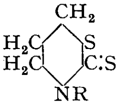

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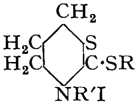


(VI.)

The synthesis of the 2-thiol derivative was effected from $\alpha\gamma$-dibromopropane through the stages phthalo-$\gamma$-bromopropylimide, $\gamma$-bromopropylamine hydrobromide (Gabriel and Weiner, *Ber.*, 1888, **21**, 2669; cf. Putochin, *Ber.*, 1926, **59**, 625), and condensation of this with carbon disulphide in the presence of sodium hydroxide (Gabriel and Lauer, *Ber.*, 1890, **23**, 87). Modifications of the original processes were usefully effected.

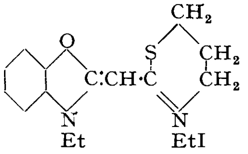
By the action of alkali and alkyl sulphate on the 2-thiol compound (IV; R = H), 2-*methylthiodihydro*-1 : 3-*thiazine* (IV; R = Me) and 2-*ethylthiodihydro*-1 : 3-*thiazine* (IV; R = Et) were prepared. By use of methyl or ethyl iodide the former base was converted into its *methiodide* (VI; R = R′ = Me), and the latter base into its *ethiodide* (VI; R = R′ = Et). During the action of ethyl iodide on the former base, a rearrangement, discussed more fully below, took place, resulting in 2-ethylthiodihydro-1 : 3-thiazine methiodide (VI; R = Et, R′ = Me). By the action of pyridine on 2-methylthiodihydro-1 : 3-thiazine methiodide (cf. Kendall, B.P. 475,647/1936), it was converted into 2-*thio*-3-*methyltetrahydro*-1 : 3-*thiazine* (V; R = Me), which gave a methiodide. 2-*Thio*-3-*ethyltetrahydro*-1 : 3-*thiazine* (V; R = Et) was similarly prepared and, from it, an ethiodide.

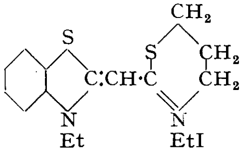
Following the work of Morton and Stubbs on benzthiazole derivatives (J., 1939, 1321), three ultra-violet absorption spectra in the present series were photographed, with the following results. In methyl-alcoholic solutions the methylthio-base (IV; R = Me) did not give a characteristic absorption band, but the thio-*N*-methyl-base (V; R = Me) and the 2-thiol compound itself each gave a definite and similar absorption curve. From analogy with other series, it may be taken for granted that the constitutions of the two methyl derivatives are as represented by formulæ (IV) and (V), and the evidence of the absorption spectra now indicates that, as in the benzthiazole group (Morton and Stubbs, *loc. cit.*), the "2-thiol-compound" is really a thione, *i.e.*, it has the constitution (V; R = H) rather than (IV; R = H), being 2-*thiotetrahydro*-1 : 3-*thiazine*.

Although Mills, Clark, and Aeschlimann regarded the constitution of the alkiodides of 2-thio-3-methyldihydrobenzthiazole as evident (J., 1923, **123**, 2362), alternatively a sulphonium structure has been formulated (I.G. Farbenind. A.-G., B.P. 423,792/1932). Up till now there has apparently been no direct comparison of the quaternary salt prepared from an alkylthio-compound with the corresponding salt prepared from the thio-*N*-alkyl-compound. The crude methiodide of (IV; R = Me) had a fairly satisfactory iodine value, but was hygroscopic and difficult to recrystallise; it had a rather lower m. p. than the easily recrystallised methiodide of (V; R = Me) (and moreover their mixed m. p. was again slightly lowered), but two recrystallisations brought its m. p. up to that of the methiodide prepared from (V; R = Me) and their mixed m. p. was now the same. Similar results were obtained with the pair of ethiodides. The very considerable drop in yield which occurred on recrystallising each of the two alkiodides prepared from (IV; R = Me or Et) renders our proof of identity incomplete. Our attempt to complete it by photographing ultra-violet absorption spectra of the crude methiodide prepared from the methylthio-compound and of the recrystallised methiodide prepared from the thio-*N*-methyl-compound was inconclusive, because in neither case was a characteristic absorption curve obtained. Sometimes very poor yields of dyes were obtained when the ether-washed alkiodides prepared from (IV; R = Me or Et) were used as starting points, so that preparation of pure alkiodides, either by recrystallisation or by passing through (V), is desirable.

We prepared methincyanines containing the dihydro-1 : 3-thiazine nucleus by condensing quaternary salts such as (VI; R = R′) with other quaternary salts containing a reactive methyl group in absolute alcoholic solution, with anhydrous potassium carbonate or triethylamine as condensing agent. Thus ether-washed 2-ethylthiodihydro-1 : 3-thiazine ethiodide with 2-methylbenzoxazole ethiodide gave (VII) but only in 4% yield; by use of purified 2-methylthiodihydro-1 : 3-thiazine methiodide the 6 : 7-benz-derivative of a methylethyl analogue of (VII) was obtained in 12% yield.

(VII.)

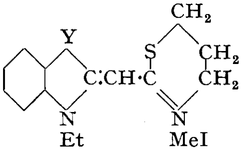


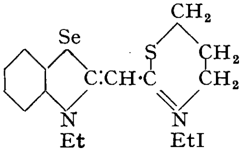


(VIII.)

Condensation of the quaternary salts (VI; R = R′) proceeded more smoothly with quaternary salts of 2-methylbenzthiazole, and of its derivatives, than it did with the corresponding benzoxazole salts. Thus there were prepared (VIII), its 4 : 5- and 6 : 7-benz- and 5-chloro-derivatives, its dimethyl analogue and the 4 : 5- and 6 : 7-benz-derivatives of that, also 6-chloro- and 6-acetamido-derivatives of a methylethyl analogue of (VIII). The yields in these nine preparations varied from 35—67%, lying between 60% and 67% in those cases where the salt (VI) had been purified. When the quaternary salt prepared by the action of ethyl iodide on (IV; R = Me) was condensed with 2-methylbenzthiazole ethiodide, the product proved to be, not (VIII), but its methylethyl analogue (IX; Y = S): this was established by an iodine determination and by m. p. determinations, a genuine specimen of (IX; Y = S) having been synthesised from (VI; R = R′ = Me) and 2-methylbenzthiazole ethiodide.

(IX.)





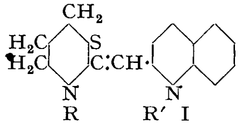
(X.)

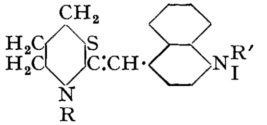
By condensing 2-methylbenzselenazole ethiodide with the ethiodide of 2-ethylthiodihydro-1 : 3-thiazine and with the methiodide of 2-methylthiodihydro-1 : 3-thiazine, respectively, there were obtained (X) and its methylethyl analogue (IX; Y = Se), the yields being 50% and 52%. Condensation of 2-methylbenzselenazole ethiodide with the quaternary salt prepared by the action of ethyl iodide on (IV; R = Me) gave the methylethyl cyanine (IX; Y = Se) and not the diethyl cyanine (X), as shown by iodine and m. p. determinations. From the two anomalous results, in the benzthiazole and benzselenazole series, it is concluded that, when ethyl iodide acts on (IV; R = Me), an interchange of alkyl groups takes place, giving 2-ethylthiodihydro-1 : 3-thiazine methiodide. The same type of rearrangement occurs when ethyl iodide acts upon 2-methylthioquinoline (Beilenson and Hamer, J., **1939**, 143) and 2-methylthiobenzthiazole (Sexton, J., **1939**, 470). Because of the possibility of such behaviour, the recommendation (Hamer, J., **1940**, 799) that, in syntheses by means of quaternary salts of alkylthio-compounds, the salts should be so chosen that the alkyl of the alkylthio-group is identical with the alkyl of the ester used for salt formation, has been adopted in the present work.

Absorption curves of methyl-alcoholic solutions of the new cyanines were plotted. The solution of (VII) is colourless with an absorption maximum at 3660 A. That of the 6 : 7-benz-derivative of its methylethyl analogue is pale yellow, with the maximum 110 A. nearer to the red end of the spectrum. Neither of these compounds sensitised a gelatinochloride photographic emulsion. On passing from the oxa-compound (VII) to the thia-compound (VIII), the maximum undergoes a bathochromic shift of 280 A. Passing from (VIII) to its 4 : 5- and 6 : 7-benz-derivatives, the shifts in the same direction are 160 and 210 A., respectively. Passing from thia- to selena-compound (VIII—X), the shift is only 60 A.

By condensing the alkiodide (VI; R = R′ = Me or Et) with quinaldine alkiodide or lepidine alkiodide, respectively, there were obtained three dyes of type (XI) and three dyes of type (XII), the yields varying from

(XI.)





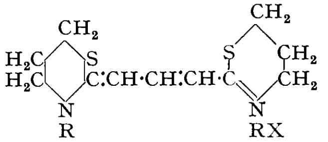
(XII.)

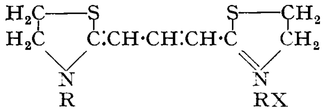
27—46% and from 30—58%. The three dyes containing the quinaldine nucleus showed little or no sensitising action, but with those which contained the lepidine nucleus all three sensitised. On passing from the thia-thiazinocyanine (VIII) to the thiazino-2′-cyanine (XI; R = R′ = Et), the effect of replacing the benzthiazole by the 2-quinoline nucleus was to cause the absorption maximum to shift 510 A. towards the region of longer wave-length; on passing from this thiazino-2′-cyanine to the thiazino-4′-cyanine (XII; R = R′ = Et), the effect of replacing the 2-quinoline nucleus by the 4-quinoline nucleus was to cause a bathochromic shift of 300 A.

2-Methyldihydro-1 : 3-thiazine (III) was prepared by Pinkus by reaction of thioacetamide with excess of α-chloro-γ-bromopropane, but the yield was only 10% (*Ber.*, 1893, **26**, 1077). As we were unable materially to improve upon this, we devised a new method: α-amino-γ-hydroxypropane, prepared from phthalo-γ-bromopropylimide by Putochin's method (*Ber.*, 1926, **59**, 625), was converted by acetic acid into *α-acetamido-γ-hydroxypropane*, whence (III) was derived by the action of phosphorus pentasulphide. The last two steps are analogous to Wenker's method of preparing α-acetamido-β-hydroxyethane and 2-methylthiazoline, respectively (*J. Amer. Chem. Soc.*, 1935, **57**, 1079). 2-Methyldihydro-1 : 3-thiazine methiodide and ethiodide were obtained as oils, which could not be solidified but were successfully used in the preparation of carbocyanines.

In a French patent which appeared after our work was well under way (I.G. Farbenind. A.-G., F.P. 850,653/1939), 2-methyldihydro-1 : 3-thiazine, prepared by the method of Pinkus, is said to have been converted into its methiodide and ethiodide which, unlike our specimens, were both described as solid substances of definite m. p., and were subjected to various cyanine condensations. For preparing methincyanines containing the simple thiazine nucleus, we prefer the method in which the starting point is the thiol- or thio-derivative (IV or V) rather than the more difficultly accessible methyl derivative (III). According to the French patent, three methincyanines were made by the latter method, namely, (VIII) and two of type (XI; R = Me, R′ = Me and Et, respectively) (examples 5, 3, and 4). The first of these is another point of disagreement, since decomposition at 238° is recorded, whereas we found m. p. 265° (decomp.); the dyes of type (XI) cannot be compared, since they were isolated as perchlorates whereas we made iodides. By condensing the methiodide and ethiodide of (III) with ethyl orthoformate in the presence of pyridine, we prepared a pair of carbocyanines (XIII; R = Me or Et), which proved to be good sensitisers for chloride emulsions. The appropriate example (no. 1) in the French patent approximates in properties to the former of our dyes. That is the only example, out of eight, in which photographic properties are recorded, although the patent purports to deal with photographic sensitisers.

(XIII.)

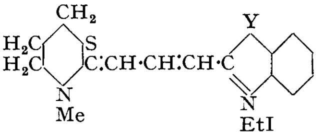




(XIV.)

The thiazinocyanines are particularly interesting as affording the first opportunity of comparing cyanines with others from which they differ only in having an extra member in the ring. In the first paper of this series, it was shown that the absorption maximum undergoes a hypsochromic shift when the benzthiazole nucleus of carbocyanines is replaced by the 2 : 4-benzthiazine nucleus (Beilenson and Hamer, J., 1942, 98). On comparing the present new dyes containing the dihydro-1 : 3-thiazine nucleus with Brooker's dyes containing the thiazoline nucleus (*J. Amer. Chem. Soc.*, 1936, **58**, 662), the shift is found to be in the opposite direction. Thus, on passing from the thiazolinocarbocyanines (XIV; R = Me or Et) to the corresponding thiazinocarbocyanines (XIII; R = Me or Et), the absorption maximum shifts 175 and 165 A., respectively, towards the region of longer wave-length. On passing from the thiazolino-2′-cyanine to the corresponding thiazino-2′-cyanine (XI; R = R′ = Et), there is again a bathochromic shift, but an exact figure cannot be quoted, because the thiazolino-2′-cyanine is peculiar in having two maxima of almost equal intensity. On passing from the thiazolino-4′-cyanine to the corresponding thiazino-4′-cyanine (XII; R = R′ = Et), the absorption maximum shifts 160 A. towards the region of longer wave-length.

By condensing the methiodide of (III) with 2-β-acetanilidovinylbenzoxazole ethiodide and with 2-β-acetanilidovinylbenzthiazole ethiodide, we obtained two unsymmetrical *carbocyanines* (XV; Y = O and S, respectively). It has been stated (F.P. 850,653) that the perchlorates of two homologous dyes were prepared from starting points of this type and that one of them was also prepared from (XVI; R = Et) and 2-methylbenzoxazole ethiodide. We prepared 2-β-*anilinovinyldihydro*-1 : 3-*thiazine methiodide* by fusion of 2-methyldihydro-1 : 3-thiazine methiodide with diphenylformamidine, and converted it into 2-β-*acetanilidovinyldihydro*-1 : 3-*thiazine methiodide* (XVI; R = Me) by the action of acetic anhydride. We were, however, unable to obtain (XVI; R = Me) by a method analogous to that recorded for (XVI; R = Et) in the French patent.



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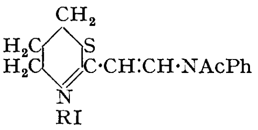
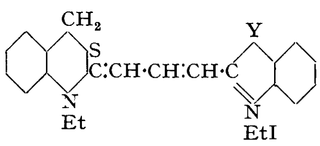


(XVI.)

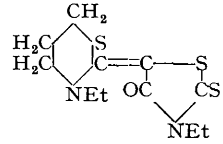


(XVII.)

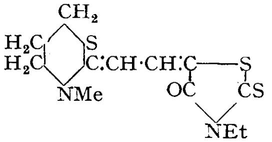
An interesting comparison is that between the two dyes (XV; Y = O and S, respectively), containing the dihydro-1 : 3-thiazine nucleus, and the two dyes (XVII; Y = O and S, respectively) containing the 2 : 4-benzthiazine nucleus, which were described by Beilenson and Hamer (*loc. cit.*). On passing from (XV; Y = O) to (XVII; Y = O) the absorption maximum undergoes a bathochromic shift of 300 A., whilst on passing from (XV; Y = S) to (XVII; Y = S) the bathochromic shift is 250 A. The fact that the two dyes of formula (XV) are methylethyl dyes whilst the two of formula (XVII) are diethyl dyes may be discounted, and the above shifts are therefore regarded as those due to replacement of the simple dihydro-1 : 3-thiazine nucleus by the 2 : 4-benzthiazine nucleus.

A couple of dyes, containing the dihydro-1 : 3-thiazine nucleus, but other than cyanines, were prepared by taking advantage of the reactive cyclic methylene group of 3-ethylrhodanine. Condensation of 3-ethylrhodanine with 2-ethylthiodihydro-1 : 3-thiazine ethiodide gave (XVIII) (cf. Kendall, B.P. 426,718/1933; Kodak Ltd., B.P. 450,958/1934), and its condensation with (XVI; R = Me) gave (XIX) (cf. Kendall, B.P. 428,359/1933; Kodak Ltd., *loc. cit.*). On passing from the diethyl compound (XVIII) to the methylethyl compound (XIX), which has an extra dimethin group in the chain, the absorption maximum shifts 830 A. towards the red. Both compounds are photographic sensitisers. For comparison we prepared a dye in which the dihydro-1 : 3-thiazine nucleus of (XIX) was replaced by the thiazoline nucleus. On passing from it to (XIX), the absorption maximum shifted 110 A. into the region of longer wave-length.

(XVIII.)



(XIX.)



## Experimental.

*Phthalo-γ-bromopropylimide.*—αγ-Dibromopropane and potassium phthalimide were heated together with mechanical stirring. Extraction with light petroleum (b. p. 40—60°) gave a 74% yield of the imide (Gabriel and Weiner, *loc. cit.*, obtained 62%) (Found for material dried in a vacuum desiccator : Br, 29·8. Calc. for $C_{11}H_{10}O_2NBr$ : Br, 29·8%).

*γ-Bromopropylamine Hydrobromide.*—Gabriel and Weiner's method (*loc. cit.*) was modified by use of acetic acid and by increasing the time of heating : the preceding imide (150 g.), hydrobromic acid (*d* 1·5; 150 c.c.), and acetic acid (75 c.c.) were refluxed for 8 hours. The hot product was poured on ice, the phthalic acid removed, and the filtrate concentrated on the water-bath under reduced pressure. The product was taken up in hot ethyl alcohol (1 c.c. per g.); the substance which crystallised from the filtered solution was ground with ether (yield, 108 g.; 89%) and used for the next stage. After recrystallisation from alcohol and ether (1 c.c. and 4 c.c. per g.), the m. p. was 161—163° (yield, 59%); Gabriel and Weiner give m. p. 162°. For analysis, the salt was dried to constant weight in a vacuum at 60—80°, which method of drying was always used, except where otherwise stated (Found : Br, 72·8. Calc. for $C_3H_9NBr_2$ : Br, 73·0%).

2-*Thiotetrahydro*-1 : 3-*thiazine* (or 2-*Thioldihydro*-1 : 3-*thiazine*).—γ-Bromopropylamine hydrobromide (35 g.; 1 mol.), in a flask cooled with ice, was treated with excess of carbon disulphide (28 c.c.; 3 mols.) and stirred while an ice-cold solution of sodium hydroxide (14·8 g.; 2·2 mols.) in water (93 c.c.) was run in; stirring was then continued for 45 minutes. After standing in the ice-chest overnight, the thio-compound was collected and washed with water (yield, 17·2 g.; 81%). After recrystallisation from absolute alcohol (15 c.c. per g.), the yield was 69% (Found : S, 47·9. Calc. for $C_4H_7NS_2$ : S, 48·1%). M. p. 129—131°; Gabriel and Lauer give m. p. 132° (*loc. cit.*). Its methyl-alcoholic solution had an absorption maximum at 2875 A.

2-*Methylthiodihydro*-1 : 3-*thiazine* (IV; R = Me).—Methyl sulphate (13·5 c.c.; 1·5 mols.) was gradually added, with vigorous shaking, to 2-thiotetrahydro-1 : 3-thiazine (24 g.; 1 mol.) dissolved in cold 20% sodium hydroxide solution (270 c.c.). The resultant oil was extracted with ether, dried with sodium sulphate, recovered, and distilled in a vacuum (yield, 13·1 g.; 50%) (Found : S, 43·4. $C_5H_9NS_2$ requires S, 43·6%). B. p. 155—160°/50 mm. Its methyl-alcoholic solution showed no characteristic absorption maximum.

2-*Ethylthiodihydro*-1 : 3-*thiazine* (IV; R = Et).—2-Thiotetrahydro-1 : 3-thiazine (8 g.; 1 mol.) was suspended in 20% sodium hydroxide solution (20 c.c.; 1·7 mols.), and ethyl sulphate (8 c.c.; 2 mols.) added, with shaking. The mixture was then heated on the water-bath for 30 minutes, with occasional shaking, and after 12 hours the oil was extracted with ether and twice vacuum-distilled (yield of colourless oil, 37%) (Found : S, 39·7. $C_6H_{11}NS_2$ requires S, 39·8%). B. p. 145—150°/40 mm.

2-*Methylthiodihydro*-1 : 3-*thiazine Methiodide* (VI; R = R′ = Me).—2-Methylthiodihydro-1 : 3-thiazine (10·95 g.; 1 mol.) and methyl iodide (9·2 c.c.; 2 mols.) were left in a sealed tube at room temperature for 3 days. The yield of ether-washed, white, hygroscopic solid, m. p. 121°, was 83% (17·9 g.). After two recrystallisations from ethyl alcohol (1·5 c.c. per g.) (yield, 36%) the m. p. was constant at 132—133° (Found for the crude product after drying in a vacuum desiccator : I, 43·6. Found for the twice recrystallised product : I, 43·9. $C_6H_{12}NIS_2$ requires I, 43·9%). By the second method, 2-thio-3-methyltetrahydro-1 : 3-thiazine (2 g.; 1 mol.) and methyl iodide (1·3 c.c.; 1·5 mols.) were sealed up together in a tube; solution occurred, with rise of temperature, and the liquid subsequently solidified to a white mass. After standing for a few hours at room temperature, the product was ground with absolute ether, being obtained in 94% yield (3·9 g.), m. p. 129°. It was recrystallised from ethyl alcohol (1·5 c.c. per g.) and obtained in 75% yield, m. p. 132° (Found for material dried in a vacuum desiccator : I, 43·95%). The mixed m. p. of the crude methiodides prepared by the two different methods was 115—116°, but the mixed m. p. of recrystallised samples was 132°.

2-*Ethylthiodihydro*-1 : 3-*thiazine Ethiodide* (VI; R = R′ = Et).—After 2-ethylthiodihydro-1 : 3-thiazine (1 mol.) and ethyl iodide (2 mols.) had been kept in a sealed tube at room temperature for 3 days, this was heated at 100° for 8 hours. The viscous liquid solidified when ground with absolute ether (78% yield). After recrystallisation from ethyl alcohol (1·2 c.c. per g.) the yield was 19% (Found for the recrystallised salt dried in a vacuum desiccator : I, 40·1. $C_8H_{16}NIS_2$ requires I, 40·0%). M. p. 98°. By the second method, 2-thio-3-ethyltetrahydro-1 : 3-thiazine (1·6 g.; 1 mol.) and ethyl iodide (1·1 mols.) were heated together in a sealed tube at 100° for 30 minutes, and the product ground with absolute ether. A 98% yield of almost colourless solid was obtained and after recrystallisation from ethyl alcohol (1·5 c.c. per g.) the yield was 50% (Found for the ether-washed product after drying in a vacuum desiccator : I, 40·15. Found for the recrystallised product : I, 40·1%). M. p. 99°.

2-*Ethylthiodihydro*-1 : 3-*thiazine Methiodide* (VI; R = Et, R′ = Me).—2-Methylthiodihydro-1 : 3-thiazine (IV; R = Me) (1 mol.) and ethyl iodide (2 mols.), when kept in a sealed tube at room temperature for 3 days, deposited an oil. After heating at 60° for 16 hours and at 100° for 24 hours, the product was brown and viscous, but refused to solidify when cooled and washed with absolute ether. Its constitution was inferred from analyses of two of its condensation products.

2-*Thio*-3-*methyltetrahydro*-1 : 3-*thiazine* (V; R = Me).—2-Methylthiodihydro-1 : 3-thiazine methiodide (10·5 g.) was boiled with pyridine (36 c.c.) for 20 minutes, and the solution poured into water (180 c.c.) and concentrated to one-third under reduced pressure. The product crystallised on cooling and was recrystallised from ethyl alcohol (26 c.c.), the yield of colourless needles, m. p. 88°, being 71% (4·03 g.) (Found for material dried in a vacuum at 50° : S, 43·8. $C_5H_9NS_2$ requires S, 43·6%). Its methyl-alcoholic solution had an absorption maximum at 2825 A.

2-*Thio*-3-*ethyltetrahydro*-1 : 3-*thiazine* (V; R = Et).—2-Ethylthiodihydro-1 : 3-thiazine ethiodide (19 g.) was boiled with pyridine (30 c.c.) for an hour, and the solution poured into water. The resultant oil solidified (67% yield). On recrystallisation from ethyl alcohol (4 c.c. per g.), the yield of almost colourless crystals, m. p. 68°, was 54% (Found for material dried in a vacuum desiccator : S, 40·0. $C_6H_{11}NS_2$ requires S, 39·8%).

*α-Amino-γ-hydroxypropane.*—This was prepared by Putochin's method (*loc. cit.*). The process of taking the aqueous solution down to dryness was repeated three times instead of twice and was carried out under reduced pressure by heating in an oil-bath. The yield was 75%, b. p. 184—186°, whereas he records an almost 90% yield.

*α-Acetamido-γ-hydroxypropane.*—α-Amino-γ-hydroxypropane (77 g.; 1 mol.) was stirred while acetic acid (65 c.c.; 1 mol.) was slowly added. The liquid was heated, in order to drive off the liberated water, until its temperature was 200°. The yield was 87% (106 g.) and this crude product was used for the next stage of the synthesis (Found : N, 12·15. $C_5H_{11}O_2N$ requires N, 12·0%).

2-*Methyldihydro*-1 : 3-*thiazine* (III).—A mixture of α-acetamido-γ-hydroxypropane (32 g.; 5 mols.) and phosphorus pentasulphide (16 g.; 1·1 mols.) was heated to start reaction. When this abated, heat was again applied, and distillation continued up to 190°. The resultant oil was distilled; the fraction, b. p. 165—175°, amounted to a 20% yield (13·5 g. from two such batches). Pinkus gives b. p. 173°/757 mm. (*loc. cit.*).

2-*Methyldihydro*-1 : 3-*thiazine Methiodide.*—2-Methyldihydro-1 : 3-thiazine (11·2 g.; 1 mol.) and methyl iodide (12 c.c.; 1·5 mols.) were mixed; reaction then occurred. After standing in a closed vessel at room temperature for 3 hours, the resultant yellow oil was washed with absolute ether, being obtained in 66% yield (16 g.).

2-*Methyldihydro*-1 : 3-*thiazine Ethiodide.*—2-Methyldihydro-1 : 3-thiazine (2 g.; 1 mol.) and ethyl iodide (3 c.c.; 2 mols.) were heated together in a sealed tube at 100° for 3 hours. After being washed with absolute ether, the yield of viscous salt was 75%.

2-*β-Anilinovinyldihydro*-1 : 3-*thiazine Methiodide.*—2-Methyldihydro-1 : 3-thiazine methiodide (7 g.; 1 mol.) and diphenylformamidine (6·1 g.; 1 mol.) were heated together in an oil-bath at 140° for 10 minutes, with frequent stirring. The melt was taken up in hot spirit (12 c.c.); on cooling, bright yellow crystals, m. p. 165°, separated in 56% yield (5·6 g.) (Found : I, 35·45. $C_{13}H_{17}N_2IS$ requires I, 35·25%).

2-*β-Acetanilidovinyldihydro*-1 : 3-*thiazine Methiodide* (XVI; R = Me).—The preceding compound (1 g.) was boiled for 10 minutes with acetic anhydride (5 c.c.). When the solution was cooled in ice, a yellow solid crystallised. After washing with ether, the yield was 18% (0·2 g.) (Found : I, 31·7. $C_{15}H_{19}ON_2IS$ requires I, 31·6%) and m. p. 180—185°.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][2-(3-*ethylbenzoxazole*)]*methincyanine Iodide* (VII).—Ether-washed 2-ethylthiodihydro-1 : 3-thiazine ethiodide (5·1 g.; 1 mol.), 2-methylbenzoxazole ethiodide (4·6 g.; 1 mol.), triethylamine (3·9 c.c.; 1 mol.), and absolute alcohol (20 c.c.) were boiled together, with stirring, for 2 minutes. The product was collected, washed with water, and crystallised from absolute alcohol (50 c.c. per g.), but the yield was only 4% (Found : I, 30·3. $C_{16}H_{21}ON_2IS$ requires I, 30·5%). The pale yellow crystals had m. p. 260° (decomp.) and gave an almost colourless methyl-alcoholic solution with absorption maximum at 3660 A.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(3-*ethyl*-6 : 7-*benzbenzoxazole*)]*methincyanine Iodide.*—Purified 2-methylthiodihydro-1 : 3-thiazine methiodide (1·83 g.; 1 mol.), 2-methyl-6 : 7-benzbenzoxazole ethiodide (2·15 g.; 1 mol.), triethylamine (1·3 c.c.; 1·5 mols.), and absolute alcohol (12 c.c.) were boiled together, with stirring, for 7 minutes. The product was collected, washed with water and ether (0·47 g. obtained), and crystallised from absolute alcohol (30 c.c.). The yield was 12% (0·35 g.) (Found : I, 27·9. $C_{19}H_{21}ON_2IS$ requires I, 28·1%). The pale pink solid, m. p. 264° (decomp.), gave a methyl-alcoholic solution with absorption maximum at 3770 A.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(3-*methylbenzthiazole*)]*methincyanine Iodide.*—This was prepared by boiling together ether-washed 2-methylthiodihydro-1 : 3-thiazine methiodide (1·45 g.; 1 mol.), 2-methylbenzthiazole methiodide (1 mol.), anhydrous potassium carbonate (180-mesh; 1·2 mols.), and absolute alcohol for 30 seconds, with hand stirring. After recrystallisation of the water-washed product from methyl alcohol (70 c.c. per g.), the yield was 55% (Found : I, 31·3. $C_{14}H_{17}N_2IS_2$ requires I, 31·4%). M. p. 283° (decomp.). A methyl-alcoholic solution of the pinkish crystals had its absorption maximum at 3920 A. The substance weakly sensitised a gelatinochloride photographic emulsion, giving a maximum at about 4150.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][2-(3-*ethylbenzthiazole*)]*methincyanine Iodide* (VIII).—This was prepared from recrystallised 2-ethylthiodihydro-1 : 3-thiazine ethiodide and 2-methylbenzthiazole ethiodide, being obtained in 67% yield after recrystallisation from methyl alcohol (33 c.c. per g.) (Found : I, 29·4. $C_{16}H_{21}N_2IS_2$ requires I, 29·4%). The buff solid had m. p. 265° (decomp.), whereas a specimen of this constitution has been described elsewhere (F.P. 850,653/1939, ex. 5) as decomposing at 238°. A methyl-alcoholic solution had its absorption maximum at 3940 A. The cyanine weakly sensitised a chloride emulsion, the maximum effect occurring at 4200 A. and sensitisation extending to 4500.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(3-*methyl*-4 : 5-*benzbenzthiazole*)]*methincyanine Iodide.*—This was prepared from ether-washed 2-methylthiodihydro-1 : 3-thiazine methiodide and 2-methyl-4 : 5-benzbenzthiazole methiodide. Heating at the reaction stage was for 3 minutes and that was the time of heating in the following condensations, except where otherwise stated. After recrystallising from methyl alcohol (65 c.c. per g.) the yield was 54% (Found : I, 27·9. $C_{18}H_{19}N_2IS_2$ requires I, 27·9%). The greenish crystals had m. p. 226° (decomp.). They weakly sensitised a chloride emulsion up to 4700 A., with a maximum at 4300.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(3-*methyl*-6 : 7-*benzbenzthiazole*)]*methincyanine Iodide.*—The 6 : 7-benz-derivative was prepared by use of 2-methyl-6 : 7-benzbenzthiazole methiodide. After recrystallisation from methyl alcohol (80 c.c. per g.), the yield was 58% (Found : I, 27·8. $C_{18}H_{19}N_2IS_2$ requires I, 27·9%). The greenish-yellow crystals had m. p. 267° (decomp.). The substance sensitised a chloride emulsion moderately to beyond 4700 A., the maximum lying at 4300.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][2-(3-*ethyl*-4 : 5-*benzbenzthiazole*)]*methincyanine Iodide.*—This was prepared from ether-washed 2-ethylthiodihydro-1 : 3-thiazine ethiodide (1·59 g.) and 2-methyl-4 : 5-benzbenzthiazole etho-*p*-toluenesulphonate, with potassium carbonate in alcohol, the time of heating being 15 minutes, with mechanical stirring. The product was dissolved in hot spirit (75 c.c.) and treated with a hot solution of potassium iodide (3 g.) in water (200 c.c.). The resultant iodide (1·46 g.) was recrystallised from methyl alcohol (50 c.c.) with addition of charcoal (0·5 g.), and was obtained in 35% yield (Found : I, 26·4. $C_{20}H_{23}N_2IS_2$ requires I, 26·3%). The greenish-yellow crystals had m. p. 238° (decomp.). The methyl-alcoholic solution had its absorption maximum at 4100 A. The substance is a fairly good sensitiser for a washed chloride emulsion, the maximum lying at 4350.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][2-(3-*ethyl*-6 : 7-*benzbenzthiazole*)]*methincyanine Iodide.*—This was prepared as above by use of 2-methyl-6 : 7-benzbenzthiazole etho-*p*-toluenesulphonate, followed by treatment with potassium iodide solution. The dye *iodide* was recrystallised from methyl alcohol (40 c.c. per g.) with addition of charcoal (0·3 g. per g.) and obtained in 43% yield (Found : I, 26·2. $C_{20}H_{23}N_2IS_2$ requires I, 26·3%). The greenish-yellow crystals had m. p. 254° (decomp.). The absorption maximum of the methyl-alcoholic solution was at 4150 A. The substance is a fairly good sensitiser for a washed chloride emulsion, the maximum lying at 4300 and sensitivity being extended past 4700.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][2-(5-*chloro*-3-*ethylbenzthiazole*)]*methincyanine Iodide*.—Ether-washed 2-ethylthiodihydro-1 : 3-thiazine ethiodide was condensed with 5-chloro-2-methylbenzthiazole ethiodide. After recrystallisation from absolute alcohol (70 c.c. per g.), the yield was 52% (Found : Cl + I, 34·7. $C_{16}H_{20}N_2ClIS_2$ requires Cl + I, 34·8%). The pinkish-yellow crystals had m. p. 251° (decomp.). The absorption maximum is at 3940 A. The salt is a fair sensitiser up to 4600, with a maximum at 4150.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(6-*chloro*-3-*ethylbenzthiazole*)]*methincyanine Iodide*.—Crystallised 2-methylthiodihydro-1 : 3-thiazine methiodide was condensed with 6-chloro-2-methylbenzthiazole ethiodide and recrystallisation was from methyl alcohol (150 c.c. per g.). The yield was 64% whether anhydrous potassium carbonate or triethylamine was used as condensing agent (Found : Cl + I, 36·0. $C_{15}H_{18}N_2S_2ClI$ requires Cl + I, 35·9%). The pinkish solid had m. p. 283° (decomp.) and gave an almost colourless methyl-alcoholic solution. It caused extremely slight sensitisation with maximum at 4100 A.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(6-*acetamido*-3-*ethylbenzthiazole*)]*methincyanine Iodide*.—Crystallised 2-methylthiodihydro-1 : 3-thiazine methiodide and 6-acetamido-2-methylbenzthiazole ethiodide were similarly condensed. After recrystallisation from methyl alcohol (135 c.c. per g.), the yields were materially the same (63% and 60%) whether potassium carbonate or triethylamine had been used as condensing agent (Found : I, 26·8. $C_{17}H_{22}ON_3IS_2$ requires I, 26·7%). The yellow crystalline substance had m. p. 279° (decomp.). The absorption maximum was at 4000 A. and the sensitising maximum at 4200, the sensitisation extending to 4600.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(3-*ethylbenzthiazole*)]*methincyanine Iodide* (IX; Y = S).—This was prepared from ether-washed 2-methylthiodihydro-1 : 3-thiazine methiodide and 2-methylbenzthiazole ethiodide in alcohol in the presence of potassium carbonate, with boiling and mechanical stirring for 10 minutes. The water-washed product was recrystallised from absolute alcohol (33 c.c. per g.) with addition of charcoal (1 g. per g.) to remove a trace of pink impurity. This caused the yield to drop from 74 to 25% (Found : S, 15·6; I, 30·4. $C_{15}H_{19}N_2IS_2$ requires S, 15·3; I, 30·35%). The buff crystals decomposed at 249°. It is a very weak sensitiser with maximum at about 4200 A.

When the salt from 2-methylthiodihydro-1 : 3-thiazine and ethyl iodide was condensed with 2-methylbenzthiazole ethiodide, the washed product, after recrystallisation from absolute alcohol (40 c.c. per g.), was obtained in 76% yield. After a second recrystallisation, an iodine determination indicated that the salt isolated is the above methylethyl, and not the diethyl, derivative (Found : I, 30·2%). This was confirmed by its m. p. and by its mixed m. p. with the above methylethyl compound.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][2-(3-*ethylbenzselenazole*)]*methincyanine Iodide* (X).—This was prepared from recrystallised 2-ethylthiodihydro-1 : 3-thiazine ethiodide and 2-methylbenzselenazole ethiodide, with potassium carbonate in alcohol, being obtained after recrystallisation from absolute alcohol (80 c.c. per g.), with addition of charcoal (0·4 g. per g.), in 50% yield. Iodine in the presence of selenium was determined as described by Hamer (*Analyst*, 1933, **58**, 26) (Found : I, 26·6. $C_{16}H_{21}N_2ISSe$ requires I, 26·5%). The greenish-yellow crystals had m. p. 264° (decomp.). The absorption maximum is at 4000 A. and the sensitising maximum at 4300, sensitivity extending beyond 4500.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(3-*ethylbenzselenazole*)]*methincyanine Iodide* (IX; Y = Se).—Prepared by condensation of ether-washed 2-methylthiodihydro-1 : 3-thiazine methiodide and 2-methylbenzselenazole ethiodide, this was obtained in 52% yield after recrystallisation from absolute alcohol (75 c.c. per g.) with addition of charcoal (0·3 g. per g.) (Found : I, 27·4. $C_{15}H_{19}N_2ISSe$ requires I, 27·3%). The yellow crystals had m. p. 271° (decomp.). It is a weak sensitiser with maximum at about 4250 A., the action extending to 4600.

When the salt prepared from 2-methylthiodihydro-1 : 3-thiazine and ethyl iodide was condensed with 2-methylbenzselenazole ethiodide, the product, after recrystallisation from absolute alcohol (40 c.c. per g.), resulted in 28% yield and an iodine determination indicated that it is the above methylethyl, and not the diethyl, derivative (Found : I, 27·1%). The m. p. and mixed m. p. were identical with that of the methylethyl cyanine, all taken simultaneously.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(1-*methylquinoline*)]*methincyanine Iodide* (XI; R = R′ = Me).—Recrystallised 2-methylthiodihydro-1 : 3-thiazine methiodide (0·97 g.; 1 mol.), quinaldine methiodide (0·95 g.; 1 mol.), triethylamine (0·7 c.c.; 1·5 mols.), and absolute alcohol (10 c.c.) were boiled together, with stirring, for 3 minutes. The product was washed with water and with ether (0·66 g. obtained). After recrystallisation from absolute alcohol (20 c.c.), the yield was 46% (0·61 g.) (Found : I, 31·9. $C_{16}H_{19}N_2IS$ requires I, 31·9%). The vermilion crystals had m. p. 225° (decomp.). Their methyl-alcoholic solution had its principal absorption maximum at 4450 and a weaker one at 4250 A.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][2-(1-*ethylquinoline*)]*methincyanine Iodide* (XI; R = Me, R′ = Et).—Prepared from crystallised 2-methylthiodihydro-1 : 3-thiazine methiodide, quinaldine ethiodide, and triethylamine in alcohol, with boiling for 7 minutes, and recrystallised from methyl alcohol (4 c.c. per g.), it was obtained in 27% yield (Found : I, 30·9. $C_{17}H_{21}N_2IS$ requires I, 30·8%). When ether-washed 2-methylthiodihydro-1 : 3-thiazine methiodide was used, the yield was only 3%. The yellow crystals had m. p. 189° (decomp.). The absorption maximum was at 4500 A. with a secondary maximum at 4300. This dye and the preceding one did not sensitise a silver chloride photographic emulsion.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][2-(1-*ethylquinoline*)]*methincyanine Iodide* (XI; R = R′ = Et).—Prepared from crystallised 2-ethylthiodihydro-1 : 3-thiazine ethiodide, quinaldine ethiodide, and triethylamine in alcohol, with boiling for 5 minutes, and recrystallised from methyl alcohol (3 c.c. per g.), the orange-yellow dye was obtained in 31% yield, but the result was negative when the ether-washed 2-ethylthiodihydro-1 : 3-thiazine ethiodide was used (Found : I, 29·9. $C_{18}H_{23}N_2IS$ requires I, 29·8%). M. p. 169° (decomp.). The principal absorption maximum was at 4450 A. with a secondary one at 4250. The dye was almost inert photographically but there was a trace of conferred sensitivity at 4700 A.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][4-(1-*methylquinoline*)]*methincyanine Iodide* (XII; R = R′ = Me).—Prepared from crystallised 2-methylthiodihydro-1 : 3-thiazine methiodide, lepidine methiodide, and triethylamine in alcohol, with 5 minutes' boiling, the product, after being washed with ether and water and recrystallised from methyl alcohol (1·5 c.c. per g.), was obtained in 38% yield. After a second recrystallisation from ethyl alcohol (15 c.c. per g.), the yield was 30% (Found : I, 32·0. $C_{16}H_{19}N_2IS$ requires I, 31·9%). The bright orange crystalline substance had m. p. 164—165° (decomp.). It sensitised a chloride emulsion weakly to 5300 A. with a maximum at 4950. Both this and the next dye, in methyl-alcoholic solution, had the absorption maximum at 4800.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][4-(1-*ethylquinoline*)]*methincyanine Iodide* (XII; R = Me, R′ = Et).—This was prepared from crystallised 2-methylthiodihydro-1 : 3-thiazine methiodide with lepidine ethiodide and triethylamine in alcohol, and recrystallised twice from ethyl alcohol (10 c.c. per g.), being obtained in 58% yield (Found : I, 30·7. $C_{17}H_{21}N_2IS$ requires I, 30·8%). The dull orange crystals had m. p. 202° (decomp.). It sensitised weakly to 5300 A. with a maximum at 4900.

[2-(3-*Ethyldihydro*-1 : 3-*thiazine*)][4-(1-*ethylquinoline*)]*methincyanine Iodide* (XII; R = R′ = Et).—Prepared from lepidine ethiodide, crystallised 2-ethylthiodihydro-1 : 3-thiazine ethiodide, and triethylamine in alcohol, the washed product, after recrystallisation from ethyl alcohol (17 c.c. per g.), was obtained in 47% yield (Found: I, 29·7. $C_{18}H_{23}N_2IS$ requires I, 29·8%). The orange crystals melted at 191° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4750 A. The dye sensitised a gelatinochloride photographic emulsion moderately well, with the maximum effect at 4950 A.

*Bis*-2-(3-*methyldihydro*-1 : 3-*thiazine*)*trimethincyanine Iodide* (XIII; R = Me).—2-Methyldihydro-1 : 3-thiazine methiodide (3 g.; 2 mols.), ethyl orthoformate (9 c.c.; 4 mols.), and pyridine (25 c.c.) were refluxed for 1¼ hours. Ether precipitated a tar from the orange reaction mixture and this changed to a red solid (0·56 g.) on treatment with water. After recrystallisation from absolute alcohol (11 c.c.), the yield was 13% (Found: I, 31·9. $C_{13}H_{21}N_2IS_2$ requires I, 32·0%). The deep red crystals had m. p. 188° (decomp.). The methyl-alcoholic solution showed a narrow absorption band with maximum at 4600 A. Towards a washed chloride emulsion the dye is a weak sensitiser with maximum about 4850; sensitisation extends from 4400 to 5200 A.

*Bis*-2-(3-*ethyldihydro*-1 : 3-*thiazine*)*trimethincyanine Iodide* (XIII; R = Et).—This was prepared from the ethiodide, heating being prolonged for 3 hours. The precipitated dye was recrystallised from absolute alcohol (30 c.c. per g.) and thus obtained in 16% yield (Found: I, 30·0. $C_{15}H_{25}N_2IS_2$ requires I, 29·9%). The deep red crystals had m. p. 243° (decomp.) and their methyl-alcoholic solution had an absorption maximum at 4600 A. A chloride emulsion was strongly sensitised from 4400 to beyond 5200 with a maximum at about 4850 A. This dye has been described as melting at 248—249° (decomp.) and showing a sensitising maximum of 5000 A. in a bromide emulsion (F.P. 850,653/1939).

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)] [2-(3-*ethylbenzoxazole*)]*trimethincyanine Iodide* (XV; Y = O).—2-Methyldihydro-1 : 3-thiazine methiodide (2·57 g.; 1 mol.), 2-β-acetanilidovinylbenzoxazole ethiodide (4·34 g.; 1 mol.), triethylamine (2 c.c.; 1·5 mols.), and absolute alcohol (20 c.c.) were boiled together, with stirring, for 5 minutes. The product was washed with water and with ether (0·9 g. obtained) and, after recrystallisation from methyl alcohol (30 c.c.), resulted in 19% yield (0·8 g.) (Found: I, 29·5. $C_{17}H_{21}ON_2IS$ requires I, 29·6%). The bright reddish-orange crystals had m. p. 270° (decomp.). The methyl-alcoholic solution had a well-defined absorption band with its maximum at 4700 A. and an inflection at 4500. It is a good sensitiser for a chloride emulsion, the maximum effect being at 5050 A.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)] [2-(3-*ethylbenzthiazole*)]*trimethincyanine Iodide* (XV; Y = S). This was prepared from 2-methyldihydro-1 : 3-thiazine methiodide, 2-β-acetanilidovinylbenzthiazole ethiodide, and triethylamine in alcohol. The washed product was first boiled out with methyl alcohol, and the residue then recrystallised from it (13 c.c. and 39 c.c. per g. taken), being obtained in 13% yield (Found: I, 28·4. $C_{17}H_{21}N_2IS_2$ requires I, 28·6%). The red crystals had m. p. 275° (decomp.). The absorption maximum was at 5050 A. and the sensitising maximum, which was conferred on a bromide emulsion, was at 5400 A. A gradual fall of sensitivity in the region 5700—6100 A., however, indicated the presence of impurity, doubtless the symmetrical thiacarbocyanine, which is an exceptionally good sensitiser. An alternative method of preparation from 2-methylbenzthiazole ethiodide, 2-β-acetanilidovinyldihydro-1 : 3-thiazine methiodide, and triethylamine in alcohol likewise gave a product which, although analytically pure, was shown by the far more delicate photographic test to contain the trace of impurity.

5 : 2′-(3′-*Ethyltetrahydro*-1′ : 3′-*thiazyl*)-3-*ethylrhodanine* (XVIII).—2-Ethylthiodihydro-1 : 3-thiazine ethiodide (1·59 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), triethylamine (2 c.c.; 1·5 mols.), and absolute alcohol (7 c.c.) were boiled together, with stirring, for 3 minutes. The water-washed product was crystallised from absolute alcohol (4·5 c.c.), after which the yield was 60% (0·87 g.). After recrystallisation from light petroleum (b. p. 80—100°) (100 c.c. per g.), the yield of bright yellow crystals, m. p. 102°, was 44% (Found after drying in a vacuum desiccator: S, 33·6. $C_{11}H_{16}ON_2S_3$ requires S, 33·4%). The absorption maximum of the methyl-alcoholic solution is at 4120 A. The substance is a good sensitiser for a washed chloride emulsion, having a maximum at 4400 and extending the sensitivity to 4800 A.

5 : 2′-(3′-*Methyltetrahydro*-1′ : 3′-*thiazyl*)*ethylidene*-3-*ethylrhodanine* (XIX).—2-β-Acetanilidovinyldihydro-1 : 3-thiazine methiodide (XV; R = Me) (1·52 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), triethylamine (0·7 c.c.; 1·1 mols.), and absolute alcohol (15 c.c.) were boiled and stirred together for 4 minutes. The product was washed with ether (0·55 g. obtained) and recrystallised from pyridine (5 c.c.), after which the yield was 13% (Found: S, 32·2. $C_{12}H_{16}ON_2S_3$ requires S, 32·0%). The dull red solid had m. p. 195° (decomp.). Its methyl-alcoholic solution had its absorption maximum at 4950 A. and an inflection at 4700. The compound sensitised an iodobromide emulsion moderately up to 5800, with a maximum at 5450 A., but reduced the original blue-sensitivity,.

5 : 2′-(3′-*Methyltetrahydrothiazolyl*)*ethylidene*-3-*ethylrhodanine*.—2-β-Anilinovinylthiazoline methiodide (1·79 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), triethylamine (1·0 c.c.; 1·5 mols.), and absolute alcohol (10 c.c.) were boiled and stirred together for 10 minutes. The product was washed with ether and with water (0·88 g. obtained) and recrystallised from acetic acid (25 c.c.), after which the yield was 52% (Found: S, 33·6. $C_{11}H_{14}ON_2S_3$ requires S, 33·6%). M. p. 219° (decomp.). A methyl-alcoholic solution of the orange-red crystals had its absorption maximum at 4840 A. The preparation of this dye and its sensitising action have been described in the patent literature (Kodak Ltd., B.P. 450,958/1934, ex. 48).

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